United States Patent Office 2,947,787 Patented Aug. 2, 1960

2,947,787

PREPARATION OF DIALKYL SULFOXIDES

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No Drawing. Filed Aug. 20, 1959, Ser. No. 834,959

13 Claims. (Cl. 260—607)

This invention relates to the preparation of dialkyl sulfoxides and more particularly to the preparation of these compounds by the direct reaction of thionyl chloride with a trialkylaluminum compound.

Heretofore, the preparation of dialkyl sulfoxides using thionyl chloride as one of the components has been limited to the use of this compound with a Grignard reagent. While a dialkyl sulfoxide can be produced by this method, the process is not entirely satisfactory for the reason that Grignard reagents are relatively expensive and are not readily available in large quantities.

It is, therefore, a principal object of this invention to provide a process which will obviate the disadvantages of the prior art processes. It is another object of my inveniton to provide a process for the production of dialkyl sulfoxides from materials which are readily available. It is another object of the present invention to provide a process for the production of dialkyl sulfoxides by a process which is simple and inexpensive to operate. Other objects and advantages of the process will become apparent as the invention is hereinafter more fully described.

To the accomplishment of the foregoing and related ends, this invention then comprises the features hereinafter fully described and particularly pointed out in the claims. The following description setting forth in detail certain illustrative embodiments of the invention, these being indicative, however, of but a few of the various ways in which the principle of the invention may be employed.

Broadly stated, the present invention comprises a process for the preparation of dialkyl sulfoxides wherein an alkylaluminum compound is dissolved in a hydrocarbon solvent, cooled, and then thionyl chloride also dissolved in a hydrocarbon solvent preferably the same solvent as used for the alkylaluminum compound is added thereto. After all the thionyl chloride has been added, the reaction mixture is heated during which period the system is maintained under an atmosphere of an inert gas. Upon completion of the reaction, the reaction mixture is cooled and the dialkyl sulfoxide recovered.

While the procedure described above is generally preferred, equally satisfactory results can be obtained by adding the alkylaluminum solution to the thionyl chloride solution.

Before proceeding with specific examples illustrating my invention, it may be well to indicate in general the nature of the materials required in the process.

Suitable trialkylaluminum compounds include trimethyl, triethyl, tripropyl, etc., aluminum compounds. I prefer to employ trialkylaluminum compounds wherein the alkyl group contains from 1 to 18 carbon atoms, but compounds can be used wherein the alkyl group contains a larger number of carbon atoms. In addition to trialkylaluminum compounds, other aluminum organo (alkylaluminum) compounds may be used, such as those identified by the general formulas AlR_2Cl and R_2AlOR

wherein the R's represent alkyl radicals containing from 1 to 18 or more carbon atoms. The alkyl groups of these compounds may be the same or different.

Suitable solvents for dissolving the trialkylaluminum compound and the thionyl chloride include aromatic and aliphatic hydrocarbons and ethers. I prefer to employ a solvent that has a boiling point sufficiently low so that it can be readily removed from the other components in the reaction mixture by distillation but high enough that losses through evaporation are not excessive. Also, if the solvent has a low boiling point it will form explosive mixtures with air readily and as a consequence the use of such a compound can be hazardous. As a rule, suitable solvents are those having boiling points within the range of about 30 to 200° C. I prefer to use solvents having boiling points within the range of about 40 to 85° C. It is not necessary to use a pure hydrocarbon as mixtures are satisfactory.

The reaction is carried out in the absence of air, and this is accomplished by maintaining the entire reaction under an atmosphere of an inert gas. Suitable gases for this purpose include any gas that will not react with any of the reactants present. This will include the noble gases and nitrogen.

The initial reaction is carried out at a relatively low temperature. Suitable and preferred temperature ranges for this initial reaction vary from —25 to 100° C. and from 0 to 30° C. respectively. Following the initial reaction, that is after all the thionyl chloride has been added, the temperature is raised. Suitable and preferred temperature ranges for this second reaction vary from 0 to 100° C. and from 30 to 80° C., respectively.

While I do not wish to be bound by any theory as to how my products are produced, I believe that the correct explanation expressed equation wise is substantially as follows:

$$AlR_3 + 3SOCl_2 \quad 3RS{=}O{-}Cl + AlCl_3$$
$$3RS{=}O{-}Cl + AlR_3 \quad 3R{-}S{=}O{-}R + AlCl_3$$

wherein R represents an alkyl radical.

The foregoing equations show that to prepare the dialkyl sulfoxide 2 moles of the trialkylaluminum compound and 3 moles of thionyl chloride are required. Generally, I prefer to employ chemically equivalent quantities.

In order to disclose the nature of the invention still more clearly, the following illustrative examples will be given in which "parts by weight" bear the same relation to "parts by volume" as do grams to cubic centimeters.

Example 1

To a reaction vessel in which the air was replaced with nitrogen was added a solution consisting of 87 parts by weight of tri-n-octyl-aluminum in 100 parts by volume of n-hexane. A solution consisting of 35.6 parts by weight of thionyl chloride in 70 parts by volume of n-hexane was then slowly added to the contents in the reaction vessel during which time the temperature was maintained between 0 and 10° C. After the addition of the thionyl chloride solution was completed, the mixture was heated to a temperature of 67° C. and then allowed to stand overnight. The reaction mixture was then poured over cracked ice (300 parts by weight) and the di-(n-octyl) sulfoxide removed from the reaction mixture by extraction with warm n-hexane. The sulfoxide was recovered from the n-hexane by evaporating the latter. A total of 42.8 parts of di-(n-octyl) sulfoxide was obtained.

Example 2

The procedure of Example 1 was followed with the exception that 25 parts of triethylaluminum was substi-

tuted for the tri-n-octylaluminum used in Example 1. A good yield of diethyl sulfoxide was obtained.

Additional examples were run in which tributyl, tripropyl, and tridodecyl aluminum were the specific trialkylaluminum compound used. In each example a good yield of the dialkyl sulfoxide was obtained.

The sulfoxides produced in accordance with my invention are particularly useful as oxidation inhibitors in lubricating oils and to raise the octane number of diesel fuels.

In the foregoing detailed description, it will be apparent that many variations may be made without departing from the spirit and scope of the invention. As for example, it will be readily apparent to those skilled in the art that suitable organic solvents are those which in addition to having a suitable boiling point are inert under the reaction conditions of the process. Many other variations will be apparent to those skilled in the art. I, therefore, intend to be limited only in accordance with the following patent claims.

I claim:

1. A method of preparing a dialkyl sulfoxide which comprises dissolving an alkylaluminum compound in an inert organic solvent maintaining the resulting solution at a temperature varying from —25 to 100° C. under an atmosphere of an inert gas, adding to said solution thionyl chloride dissolved in an inert organic solvent, heating the resulting mixture to a temperature varying from 0 to 100° C., cooling said mixture and then recovering the dialkyl sulfoxide.

2. A method of preparing a dialkyl sulfoxide which comprises dissolving an alkylaluminum compound in an inert organic solvent maintaining the resulting solution

at a temperature varying from 0 to 30° C. and under an atmosphere of an inert gas, adding to said solution thionyl chloride dissolved in an inert organic solvent, heating the resulting mixture to a temperature varying from 30 to 80° C., cooling said mixture and then recovering the dialkyl sulfoxide.

3. The method of claim 1 wherein the alkylaluminum compound is a trialkylaluminum compound.

4. The method of claim 3 wherein the alkylaluminum compound is trialkylaluminum compound, wherein the alkyl groups of said trialkylaluminum contains from 1 to 18 carbon atoms.

5. The method of claim 4 wherein the alkylaluminum compound is tri-n-octyl-aluminum.

6. The method of claim 4 wherein the alkylaluminum compound is triethylaluminum.

7. The method of claim 4 wherein the alkylaluminum compound is tributylaluminum.

8. The method of claim 4 wherein the alkylaluminum compound is tripropylaluminum.

9. The method of claim 4 wherein the alkylaluminum compound is tridodecylaluminum.

10. The method of claim 1 wherein the alkylaluminum compound is a dialkylaluminum alkoxide.

11. The method of claim 10 in which the alkylaluminum compound is dihexyaluminum hexoxide.

12. The method of claim 1 wherein the alkylaluminum compound is a dialkylaluminum chloride.

13. The method of claim 12 in which the alkylaluminum compound is dihexylaluminum chloride.

No references cited.